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RESONANCE ELECTRON SCATTERING BY O<sub>2</sub>  
MONOLAYERS ON GRAPHITE: REINTERPRETED

By  
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Electron angular distributions of inelastic electron scattering from O<sub>2</sub> physisorbed on graphite have been studied extensively by Palmer and co-workers. Their results have been published in more than eight papers over the past four years and summarized in two recent review articles. We have reinterpreted their data and in some aspects come to different conclusions.

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# Resonance Electron Scattering by O<sub>2</sub> Monolayers on Graphite: Reinterpreted

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## 1. Introduction

Both electron stimulated desorption (ESD) and inelastic electron scattering (IES) are enhanced strongly by anion resonant states. Occasionally, peak features observed in ESD and IES arise from the same anion resonant states. IED, however, unlike ESD, provides information on the symmetry of the anion resonant states through the angular distributions of the inelastically scattered electrons. Such electron angular distributions from O<sub>2</sub> on graphite have been studied extensively by Palmer and co-workers. Their results have been published in more than eight papers over the past four years [1-8] and summarized in two recent review articles [7,8].

On graphite, O<sub>2</sub> can be prepared in either the  $\delta$  or  $\zeta$  phase, where the molecules lie either parallel ( $\delta$  phase) or perpendicular ( $\zeta$  phase) to the graphite surface [9]. The excitation profile of the  $X(\frac{1}{2}^+g)-a(\frac{1}{2}^+g)$  electronic transition exhibits two peaks at 6 and 14 eV for the  $\delta$  phase and just one peak at 8 eV for the  $\zeta$  phase [7]. Palmer and co-workers assigned these 6 and 8 eV peaks to the same  ${}^2\Pi_g$  resonant state and attributed the 2-eV shift of the peak energies in the  $\delta$  and  $\zeta$  phases to multiple electron scattering in the solid [3]. No assignment was made for the 14 eV feature. In this paper, we propose an alternative interpretation for the origin of the 6 and 8 eV peaks and assign the 14 eV peak.

The 6, 8, and 14 eV peak features have been observed also in the ESD of O<sup>-</sup> ions from O<sub>2</sub> films and O<sub>2</sub> on rare gas films, and attributed to the  ${}^2\Pi_g(6\text{eV})$ ,  ${}^2\Sigma^+_g(8\text{eV})$ , and  ${}^2\Sigma^+_u(14\text{eV})$  resonant states, respectively [10]. Excitation to the  ${}^2\Sigma^+_g$  and  ${}^2\Sigma^+_u$  states from the O<sub>2</sub> ground state is symmetry forbidden in the gas phase but is allowed in the condensed phase when the cylindrical symmetry of the O<sub>2</sub> is relaxed by interaction with the surrounding [11]. Recent ESD studies for O<sub>2</sub> clusters clearly demonstrated that the 8 and 14 eV peaks arise from the "symmetry-forbidden" states [12]. Furthermore, in the gas phase, the symmetries of  ${}^2\Pi_g$  and  ${}^2\Sigma^+_g$  for the 6 and 8 eV peaks have been established experimentally based on the angular distribution of O<sup>-</sup> ions resulting from electron impact on O<sub>2</sub> in the ground state and the  ${}^1A_g$  excited state respectively [13,14]. These assignments are completely in line with theoretical calculations [15] and analysis [11].

## 2. Origin of the 6, 8, and 14 eV peaks in the X-a excitation

The question here is: Do the 6, 8, and 14 eV peaks observed in the X-a excitation profile arise from the same  ${}^2\Pi_g(6\text{eV})$ ,

${}^2\Sigma^+_g(8\text{eV})$ , and  ${}^2\Sigma^+_u(14\text{eV})$  resonant states as those observed in the above experiments? We shall answer this question by examining the angular distributions of inelastically scattered electrons and the electron attachment selectivity observed by Palmer and co-workers [1-8].

${}^2\Pi_g(6\text{eV})$ : The  ${}^2\Pi_g$  state was observed at 6 eV in the v=0-1 vibrational excitation profile [7]. The angular distribution of inelastically scattered electrons at incident electron energy  $E_i=6.5\text{eV}$  for the X-a excitation is almost identical to that for the v=0-1 excitation [7]. This agreement is observed for both the  $\delta$  and  $\zeta$  phases, suggesting strongly that the 6 eV peaks in the X-a and v=0-1 excitation profiles arise from the same  ${}^2\Pi_g$  state. This may be the most important finding of the present paper.

${}^2\Sigma^+_g(8\text{eV})$ : The emitted electrons from the  ${}^2\Sigma^+_g$  state decaying into the  $a(\frac{1}{2}^+g)$  state have  $\delta_g$  symmetry. Therefore, the angular distribution of emitted electrons from this state for the  $\zeta$  phase must be  $\sin^2\theta$  for small  $\theta$ , where  $\theta$  is the angle from the direction normal to the graphite surface. This  $\sin^2\theta$  dependence agrees with experimental results [5]. Further supporting evidence: The 8 eV feature appears in the X-a excitation profile for both the  $\delta$  and  $\zeta$  phases. (Although there is no discernible peak at 8 eV in the  $\delta$  phase, there is a broad shoulder which cannot be accounted for by the 6-eV resonance alone. The 6-eV resonance, which was observed in the v=0-1 excitation, does not have such an extended tail [7].) The 8 eV intensity for the  $\zeta$  phase is stronger than that for the  $\delta$  phase [7]. This non-selectivity and relative intensity can be explained, if the 8 eV feature arises from the  ${}^2\Sigma^+_g$  resonant state.

${}^2\Sigma^+_u(14\text{eV})$ : The angular distribution of the inelastically scattered electrons at 14 eV is consistent with the  ${}^2\Sigma^+_u$  symmetry [16]. Further supporting evidence: The 14 eV feature observed in the X-a excitation for the  $\delta$  phase disappears for the  $\zeta$  phase. Likewise, the  ${}^4\Sigma^+_u(3\text{eV})$  feature observed in the v=0-1 excitation for the  $\delta$  phase disappears for the  $\zeta$  phase [7]. This parallel behavior is expected, if the 14 eV feature arises from the  ${}^2\Sigma^+_u$  resonant state.

Based on the above, we conclude that the 6, 8, and 14 eV peaks observed in the X-a excitation profile indeed arise from the same  ${}^2\Pi_g(6\text{eV})$ ,  ${}^2\Sigma^+_g(8\text{eV})$ , and  ${}^2\Sigma^+_u(14\text{eV})$  states as those observed in ESD and other experiments. This conclusion disagrees with the assignment made by Palmer and co-workers who attributed the 6 and 8 eV peaks to the  ${}^2\Pi_g$  state.

## 3. The ${}^2\Pi_g$ intermediate state in the solid

What happened to the  ${}^2\Pi_g$  state in the solid? In the gas phase, the X-a electronic excitation proceeds via the  $O_2^-(^1\Pi_g)$  intermediate state at least for incident electron energies less than 5 eV [17]. This intermediate state should be differentiated from the  $O_2^-(1\pi_g)^{-1}\pi_g$  shape resonance peaked around 0.2 eV [18]. The latter has the  $1\pi_g$  component predominant within the molecular region and a negligible amplitude outside this region, while the former has comparable amplitudes in both regions. Theoretical calculations [19]

predict that this non-resonant  $2\eta_q$  intermediate state produces a very broad peak (FWHM=10eV), if there is one, in the X- $\alpha$  excitation function.

The non-resonant  $2\eta_q$  scattering, unlike the resonant  $2\eta_q$  scattering, is expected to be perturbed strongly when  $O_2$  is condensed. In fact, there is ample evidence for quenching of this non-resonant  $2\eta_q$  intermediate state in condensed phase:

(a) The observed threshold energy (3.0 eV) is delayed by 2.1 eV from the expected threshold energy of 0.9 eV [7,20].

(b) The angular distribution of inelastically scattered electrons at  $E_i=6$  eV indicates  $2\eta_q$  symmetry rather than  $2\eta_g$  symmetry, as was argued in Sec. 2.

(c) The observed features are too sharp (FWHM=4eV) to arise from non-resonant  $2\eta_q$  scattering. The latter should have either no peak or a very broad peak with FWHM=10 eV.

To sum up, the non-resonant  $2\eta_q$  intermediate state is quenched upon condensation and hence cannot be assigned to the 6 and 8 eV features.

#### 4. Resonance energy shift due to multiple electron scattering

Palmer and co-workers offered two reasons for the 2-eV shift of the " $2\eta_g$ " resonance peaks [3,7]:

- (1) theoretical calculations assuming the  $2\eta_q$  symmetry and
- (2) the similarity of the angular distributions for  $E_i=6.5$  and 8.5 eV.

Item (1): The assumption of the  $2\eta_q$  symmetry is not valid as argued in Sections 2 and 3. This explains partly why their theoretical calculations did not agree well with the experimental data [3,7].

Item (2): Although the angular distributions for  $E_i=6.5$  and 8.5 eV are similar to each other for the  $\delta$  phase, those for the  $\epsilon$  phase are quite different. The only common feature between them is that both decrease toward the normal direction. In short, there is no evidence to support the 2-eV shift of the " $2\eta_g$ " resonance.

#### 5. A concluding remark

Palmer and co-workers assigned the 6 and 8 eV peaks, observed in the X- $\alpha$  excitation, to the  $2\eta_q$  resonance and attributed the 2-eV shift of the peak energies in the  $\delta$  and  $\epsilon$  phases to multiple electron scattering in the solid. Based on this single investigation, they claimed that multiple electron scattering can substantially shift resonance energies and warned electron spectroscopists who study adsorbed molecules to be aware of this possibility [3,7]. Moreover, these authors repeatedly suggested this possibility to explain experimental results obtained by others [3,8]. Because of the Palmer and co-workers' claim, other authors considered (although did not adopt) this possibility for an explanation of their results [21]. This paper has demonstrated clearly that the Palmer and co-workers' claim is unfounded at least for the cases studied so far.

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